

AFOSR 68-1244

AD620169

BOSTON COLLEGE
CHESTNUT HILL, MASSACHUSETTS 0216.

THE MILD FLUORINATION OF NITROGEN COMPOUNDS
AF-AFOSR-62-464

by
Robert F. O'Malley
Alan M. Phipps
Bernard M. Halpin
Edward M. McCarron

Office of Aerospace Research
for the period 1 September 1962 to 31 August 1965

FINAL REPORT

ARPA PROJECT CODE No. 9100

ARPA Order No. 350-62

Reproduced by the
CLEARINGHOUSE
for Federal Scientific & Technical
Information Springfield Va 22151

~~Distribution of this~~
document is unlimited.

33

INTRODUCTION

The purpose of this research was to investigate the mild fluorination of nitrogen compounds, especially those containing the N-N bond. The first method to be investigated was the electrolysis of molten hydrazinium difluoride.

Later a study of possible electrolytic fluorinations in solvents other than hydrogen fluoride was begun. Reports by Schmidt and Schmidt (1,2) of successful applications of this method to unsaturated organic systems prompted this investigation.

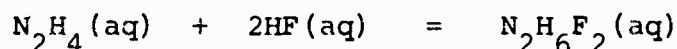
A consideration of direct fluorination at low temperatures in a solution or dispersion was also begun.

PART I

ELECTROLYSIS OF HYDRAZINIUM DIFLUORIDE

Hydrazinium difluoride, $N_2H_6F_2$

Hydrazinium difluoride was first described by Curtius and Schulz (3), who prepared crystals of the compound by evaporating an aqueous solution of hydrazine hydrate and hydrofluoric acid.



In another preparation they precipitated the salt from an alcoholic solution with ether. Subsequent investigators, usually used essentially the same methods. Kronberg and Harker (4) made the compound from a water solution containing hydrazine and hydrofluoric acid in a 1:2 molar ratio. The solution was allowed to evaporate slowly over sulfuric acid in a vacuum desiccator. Fackler (5) added the stoichiometric quantity of 42% hydrofluoric acid to a solution of hydrazine hydrate in absolute alcohol. The desired product precipitated immediately and was air-dried for two days and stored in a desiccator over magnesium perchlorate.

Deeley and Richards (6) added a 50% solution of hydrazine hydrate dropwise to a 40% hydrofluoric acid solution. The crystals that formed were recrystallized from aqueous alcohol. The product was dried in a vacuum desiccator.

Hydrazinium difluoride was prepared by Snyder and Decius (7) by titration of hydrazine monohydrate with hydrofluoric acid. A slight excess of acid was used; the product was recrystallized from an aqueous solution.

Bock (8) dissolved hydrazine dihydrochloride in liquid anhydrous hydrogen fluoride. Hydrogen chloride was evolved quantitatively and a product identified as $N_2H_4 \cdot 4HF$ was obtained. This compound slowly evolved hydrogen fluoride when kept over solid potassium hydroxide. Hydrazinium difluoride sublimed from it at 10^{-4} Torr.

The salt was described by Curtius and Schulz (3) as a white crystalline solid. It melted at $105^\circ C$ and, in addition, appeared to sublime undecomposed. Fackler's careful determination of the melting point by the capillary tube method gave $103.4^\circ C$ (5). It is highly hygroscopic (6).

An x-ray analysis (4) of the salt showed that hydrazinium ions are present which form linear hydrogen bonds to fluoride ions at the corners of an elongated octahedron. The N-N and N-H...F bond distances were reported as 1.42 \AA and 2.62 \AA , respectively. A proton and fluorine magnetic resonance spectra (6) led to the assignment of an N-H bond distance of $1.075 \pm 0.02 \text{ \AA}$ compared to 1.03 \AA in ammonium chloride and the difference was attributed to very strong N-H...F hydrogen bonds. The F...H distance was found to be $1.542 \pm 0.01 \text{ \AA}$ which leads to an N-H...F distance of $2.62 \pm 0.03 \text{ \AA}$ in good agreement with the x-ray value of $2.62 \pm 0.02 \text{ \AA}$.

The N-H-H angle is 103° (9).

From the crystal structure it is clear that the crystal contains $\text{N}_2\text{H}_6^{2+}$ and F^- ions, since the two ends of the hydrazine molecule are structurally equivalent and the shortest atoms in the HF_2^- ion in KHF_2 is 2.26 \AA (10). The infrared spectrum of $\text{N}_2\text{H}_6\text{F}_2$ was obtained by Snyder and Decius (11) at -180° . The sample was prepared for measurement by sublimation onto a transparent window cooled to near liquid nitrogen temperature.

Previously sublimed $\text{N}_2\text{H}_6\text{F}_2$ was refluxed for 16 hours with ether (6); the hydrazine content remained constant. The reaction of fluorine with solid hydrazinium difluoride at room temperature (12) produced nitrogen as the principal product with only small quantities of nitrogen trifluoride.

Preparation of hydrazinium difluoride

Aqueous solutions containing the stoichiometric quantity of hydrazine hydrate (Matheson, Coleman and Bell) were added dropwise, with stirring, to 49% hydrofluoric acid (Mallinckrodt Chemical Corp.) in polyethylene beakers, cooled with ice water. The crystals which formed were collected on a polyethylene Buechner funnel, washed with aqueous ethanol and stored in a vacuum desiccator over P_4O_{10} . In a typical preparation, 51.0 ml (1.05 mole) of hydrazine hydrate was added to 70.0 ml of 49% hydrofluoric acid (2.04 moles of HF). Yields of 90% or higher were obtained.

The melting point of thoroughly dried material was 104-105°C. Occasionally material which had been stored for extended periods of time was recrystallized from aqueous ethanol.

Analysis

Samples of the salt were analyzed by an indirect iodate method of Bray and Cuy (13, 14). The method was based on the oxidation of hydrazine to nitrogen by iodate in acid solution. An excess of standard potassium iodate solution was added and the excess determined by titration with standard sodium thiosulfate solution. $6H^+ + 5I^- + IO_3^- = 3I_2 + 3H_2O$ Iodine was also formed by the reduction of iodate by hydrazine: $4H^+ + 5N_2H_4 + 4IO_3^- = 5N_2 + 2I_2 + 12H_2O$. The total amount of iodine formed by the two reactions was involved in the titration with sodium thiosulfate.

A sample of the salt weighing approximately 0.5 g was dissolved in water and the solution diluted to 100.0 ml. A 10.00 ml aliquot was used for the titration. To 10 ml of $6NH_2SO_4$ in a stoppered Erlenmeyer flask, 50.00 ml of standard 0.1N KIO_3 was added. The ten-ml aliquot containing $N_2H_6F_2$ was added and the mixture allowed to stand for 10 minutes. After the addition of 3 g of potassium iodide in 10 ml of water to the flask, the excess iodine was titrated with standard thiosulfate.

Samples containing 99.7-99.9% $N_2H_6F_2$ were typical. When

the analysis was low, additional drying in a vacuum desiccator over sulfuric acid or Drierite led to products of over 99% purity.

One sample of hydrazinium difluoride, which had been recrystallized from ethanol and dried in vacuum over P_4O_{10} , was analyzed for its fluorine content by the lithium fluoride method of Caley and Kahle (15). An equal volume of a 3% solution of lithium chloride in 95% ethanol was added to an aqueous solution of the fluoride. The lithium fluoride precipitate was collected on a filter, dried at $110^{\circ}C$ and weighed. The sample contained 52.8% fluorine (theoretical for $N_2H_6F_2$: 52.73%).

Electrolysis Apparatus

Several types of apparatus were used for the electrolysis of molten hydrazinium difluoride. The type and arrangement of electrodes as well as the materials of construction were altered in the various modifications.

Cell Number 1 The first apparatus was cylindrical; the cell body was of monel and served as the cathode. A nickel rod served as the anode; it was shielded from the cathode by a monel shield. Figure 1 is a diagram of the cell.

The electrolysis of ammonium bifluoride was first conducted in the apparatus. The electrolysis proceeded essentially as described by Ruff, Fischer and Luft (16) and

ELECTROLYSIS CELL

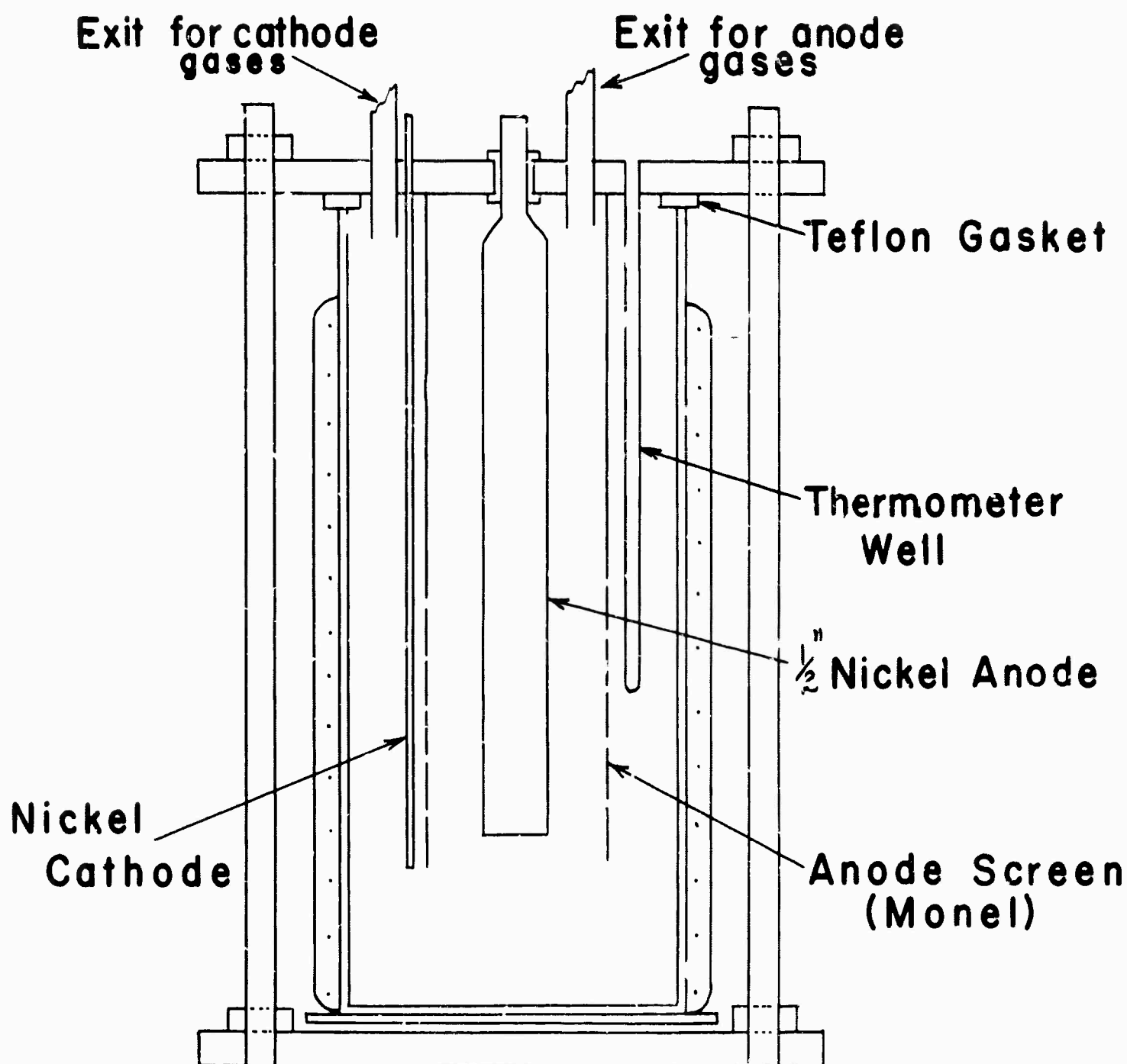


Figure 1

d Muettertities (17). The electrolysis was run at 135°C with a potential of 5.0-7.0 volts and a current of 1.0-5.0 amps. A long induction period and accumulation of a green deposit (most likely NiF_2) on the anode were observed. When the electrolysis was run without a separator between the electrodes, slight explosions occurred in the early stages of the electrolysis. Nitrogen trifluoride was identified as an anode product by an infrared analysis.

Difficulties encountered with the apparatus included plugging of the exit tubes by a solid which sublimed from the melt, difficulty in obtaining a completely molten system and low conductivity when a separator was used between the anode and cathode.

Cell Number 2 A smaller cylindrical cell was constructed from copper pipe. For many of the experiments a Teflon liner was placed in the copper cylinder. The Teflon liner was made by cutting the top portion from a commercial FEP Teflon 1-pint bottle. The liner was used to eliminate any possible interferences of side effects from the cell body.

A six-inch piece of copper pipe three inches in diameter with a wall thickness of 1/16 in. to which a disk was silver soldered provided a suitable cell body. It was heated by nichrome wire wound around it and covered with asbestos. The Teflon liner fit snugly in the cell.

The anode and cathode were attached to the cover plate

with Teflon insulators. The anode was a nickel rod, 1/2 inch in diameter and five inches in length. The cathode was a two inch by four inch nickel plate bent into a semi-cylindrical shape. With the changes noted, the apparatus resembled that in Figure 1.

Cell Number 3 The last type of cell used was a slightly modified version of the cell described by H. H. Rogers (18). The narrow rectangular container provided electrodes with large surface area. Initial experiments with molten ammonium bifluoride produced good yields of nitrogen trifluoride. It was unsatisfactory for $N_2H_6F_2$ because of extensive thermal decomposition.

Materials of Construction

The first cell was constructed of monel metal, the second of copper and the third of stainless steel. Stainless steel and copper were not suitable because the thermal decomposition of $N_2H_6F_2$ was catalyzed by it. The decomposition by monel metal was less marked, if it occurred at all.

The cells lined with Teflon were most suitable. No signs of thermal decomposition were in evidence. The Teflon liners eventually broke or were melted in spots, but they held up long enough for useful electrolyses.

Electrolysis

Table 1 is a summary of ten of the electrolysis experiments which were conducted.

TABLE 1

<u>Run</u>	<u>Cell</u>	<u>Potential (volt)</u>	<u>Current (amp)</u>	<u>Time</u>	<u>Temp.</u>
1	1	4.8 - 6.6	3.0 - 9.0	7	175
2	2	6.0 - 8.2	4.0 - 6.0	5	170
3	2	6.0 - 10.0	5.0 - 6.0	37	175
4	2	8.4 - 9.8	4.0 - 5.0	6	160
5	2	4.8 - 5.0	0.6 - 1.4	7	160
6	2	4.6 - 5.0	0.6 - 1.8	40	170
7	2	6.0 - 10.0	4.2 - 6.0	18	170
8	2	7.2 - 12.0	5.2 - 5.8	11	175
9	2	5.8 - 12.0	4.8 - 6.0	33	170
10	2	6.0 - 10.0	3.8 - 5.8	36	172

In all but run No. 10 only nitrogen was detected in the anode gas. An infrared curve from run No. 10 showed the presence of a small quantity (less than 1%) of nitrogen trifluoride.

These observations are in agreement with those reported by Schmeisser and Sartori (19). The results of their investigation appeared during our work. Few experimental details were included in the report.

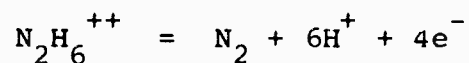
The results are also similar to those observed when fluorine was passed over hydrazinium difluoride at room temperature (12). The principal product was nitrogen, along with a small quantity of nitrogen trifluoride.

Three mechanisms have been proposed (20) for the electrochemical fluorination of organic compounds in the Simons' cell. They are: 1. the formation of fluorine with subsequent fluorination of the organic compound. 2. the formation of a higher nickel fluoride on the surface of the anode, which then acts as the fluorinating agent. 3. the oxidation of the organic species to a reactive form with subsequent reaction with hydrogen fluoride or fluoride ions. The first mechanism is the more generally accepted, but oxidation of the organic species undoubtedly often occurs, but is not observed because of the reaction with fluorine which predominates.

Applying the first of these mechanisms here, the prior formation of fluorine with subsequent fluorination of hydrazinium ions seems more likely to form nitrogen and hydrogen fluoride.

No means of detecting the second possibility are available; the products would be the same as those from mechanism 1.

The third mechanism is more applicable here. The formation of nitrogen at the anode may have been the result of the oxidation of the hydrazinium ion by a two electron per nitrogen oxidation.



The anodic oxidation of hydrazine has been studied in

aqueous solution by voltammetry (21) and chronopotentiometry (22).

The presence of nitrogen trifluoride among the products of the anodic reaction may have been due to the presence of ammonium ions, formed by thermal decomposition of hydrazinium difluoride. The nitrogen trifluoride was evident in those electrolyses conducted in metal containers which catalyzed the thermal decomposition. Catalytic decomposition was observed during electrolysis in aqueous solution (22). There is no evidence to support the view that any product other than nitrogen is formed from the hydrazinium ion at the anode during the electrolysis.

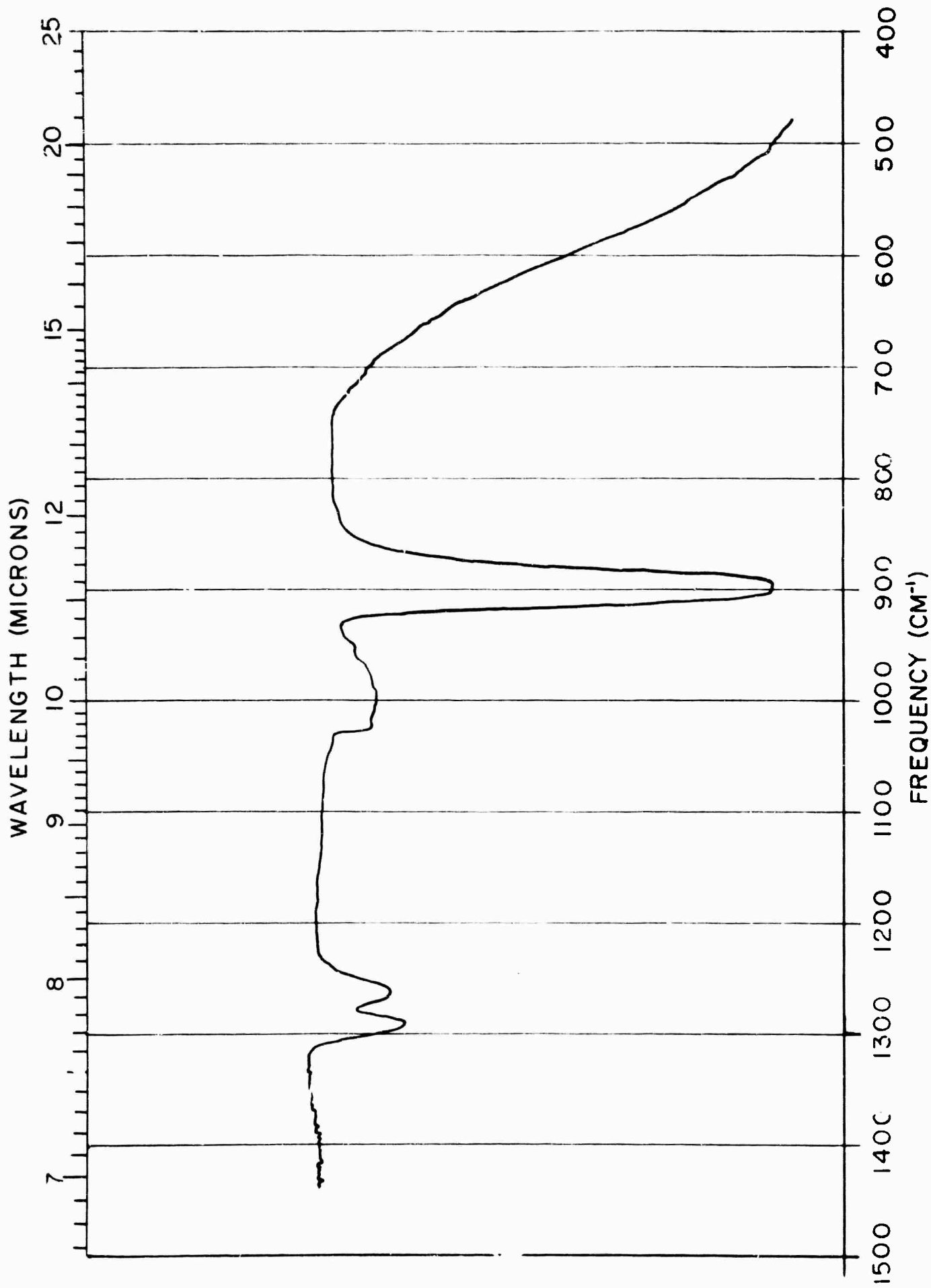
Details of the work reported in the paper of Schmeisser and Sartori (19), were found in the dissertation of F. Huber (23).^{*} The essential difference in their work was that solutions of hydrazinium difluoride in anhydrous hydrogen fluoride were electrolyzed. A solution of 350 g of hydrazinium difluoride in 2.5 liters of anhydrous hydrogen fluoride was electrolyzed in a typical experiment. The apparatus was of the Simons type, with several closely spaced anodes and cathodes. The exit gases were allowed to mix. The body of the cell was constructed of plastic. The products contained significant quantities of carbon tetrafluoride, carbonyl

^{*} Several efforts to obtain a copy of this dissertation before our work was completed failed. A copy arrived one year after our last experiment.

fluoride and nitrogen trifluoride. Ammonia was also detected in small quantities.

In our work no nitrogen trifluoride was observed when a Teflon lined cell was used. When a copper cell was used nitrogen trifluoride was detected.

Figure 2 is an infrared curve showing the presence of nitrogen trifluoride as a minor constituent of the anode gas from one electrolysis in the copper apparatus.



PART II

ELECTROLYSIS OF POTASSIUM HYDROGEN FLUORIDE SOLUTIONS IN GLACIAL ACETIC ACID

Introduction

The possibility that fluorination may be accomplished by electrolysis in a solvent other than hydrogen fluoride was first suggested by Schmidt and Schmidt (1). They reported the addition of fluorine to the double bond in 1,1-diphenylethylene by electrolysis of a solution of potassium hydrogen fluoride in glacial acetic acid, when the hydrocarbon was confined near the anode. Yields up to 70% were claimed.

The electrolysis (2) was conducted in a glass U-tube which was separated into two compartments by a glass frit. A current density of 1 - 100 MA/cm² at a potential of 5 - 30V was used. In one experiment 5.12 g of 1,1-diphenylethylene was confined to the anode compartment while the electrolysis of a solution containing 2.8 g of potassium hydrogen fluoride in 50 ml of glacial acetic acid was continued for 24 hours. A 27% yield of compound melting at 66° and identified as 1,1-diphenyl-1,2-difluoroethane was reported.

In a second experiment a 70% yield of 1,1-diphenyl-1,2-difluoroethane was obtained by electrolysis of a

solution containing 10 g KHF_2 and 10 g 1,1-diphenyl-ethylene in 80 ml of glacial acetic acid.

The addition of fluorine to the double bond in 1,1-diphenyl-ethylene had first been reported by Dimroth and Bockemuller (24) who used both lead tetraacetate and anhydrous hydrogen fluoride and iodobenzene difluoride as fluorinating agents. The product melted at 66° and was assumed to be 1,1-diphenyl-1,2-difluoroethane. Bornstein and coworkers (25) showed, however, that under the conditions of both methods of synthesis, a rearrangement occurred and the difluoride was, in fact, 1,1-difluoro-1,2 diphenylethane, ν, α -difluorobibenzyl. Schmidt and Schmidt assumed that their product was that expected from symmetrical addition, but after a reexamination of their product (26) agreed with the conclusions of Bornstein.

In any event, Schmidt and Schmidt described an apparently successful fluorination by electrolysis of a KHF_2 solution in glacial acetic acid. They claimed current efficiencies up to 92% (2).

Anhydrous acetic acid had been suggested as a possible solvent for fluorinations by Fredenhagen and Cadenback (6) because of relative stability toward fluorine. They had found no example of its use for this purpose, however. Schmidt and Schmidt assumed that the resistance of oxidation of acetic acid was such that it would act as an indifferent solvent during the electrolysis of an ionic fluoride, a

smooth secondary reaction of fluorine with the organic solute would occur.

Judging from the high value of standard oxidation potential of fluoride in an aqueous solution (-2.87 volt), the possibility of producing fluorine by electrolysis in glacial acetic acid seems unlikely. The ease with which the Kolbe electrochemical synthesis of hydrocarbons occurs (28) also casts doubt on the proposed mechanism of the fluorination.

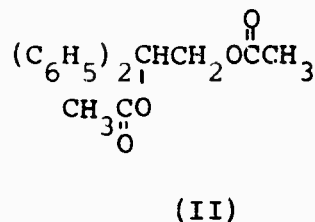
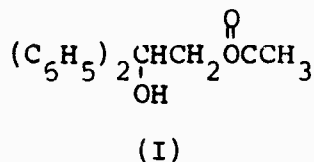
Since the fluorination was apparently achieved, however, the method seemed worthy of further investigation. The fluorination of 1,1-diphenyl-ethylene had been extensively investigated by Bornstein and his students (25,24) at Boston College. An investigation of this electrolytic process was undertaken. If the addition of fluorine to the double bond in organic compounds can be accomplished, the application of the method to nitrogen compounds is a likely extension.

Electrolytic Acetoxylation

Despite many attempts under a variety of conditions and in several different types of apparatus, we have not been able to repeat the work of Schmidt and Schmidt.

The principal products which were isolated were 2-O-acetyl 1,1-diphenylethylene glycol(I) and its corresponding

diacetate (II)



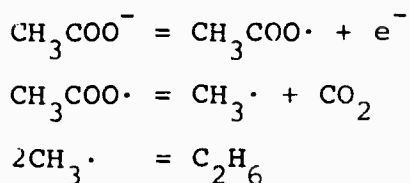
During our investigation, Mango and Bonner (30) reported on an investigation of the electrolysis of 1,1-diphenylethylene in glacial acetic acid solutions containing sodium acetate. The principal products of their electrolyses were identical to those obtained by us in the electrolysis of potassium hydrogen fluoride solutions in acetic acid.

Mechanism of Acetoxylation

Whether a solution containing sodium acetate as the electrolyte or a solution containing potassium hydrogen fluoride as the electrolyte is considered, the reaction seems to have proceeded through a reaction involving acetate ions. The presence of the hydrogen fluoride ion could lead to an increase in the acetate ion concentration over that of pure

acetic acid by the reaction: $\text{HF}_2^- + \text{CH}_3\text{COOH} = 2\text{HF} + \text{CH}_3\text{COO}^-$.

A search for a possible mechanism for the reaction leads first to a consideration of the well-known Kolbe electrolytic synthesis (31). The Kolbe synthesis is usually done in aqueous solution or in methanol solution. A few studies of the reaction in anhydrous systems (28,32) have been reported, however. The results of the electrolysis of salts of fatty acids in solutions of the anhydrous acids leads principally to the production of the corresponding alkane. Thus the electrolysis of sodium acetate solutions in anhydrous acetic acid produced ethane as the chief anodic gaseous product. The mechanism of this reaction (33) is generally believed to involve the decomposition of the first-formed acetoxy radical.



The possible steps in the mechanism have been discussed by Mango and Bonner (30). That the acetoxy radical could attack the double bond in 1,1-diphenylethylene is a tempting mechanism. Szwarc (34) has shown, however, that the lifetime of the acetoxy radical is only $10^{-9} - 10^{-10}$ sec. He has further suggested that such radicals react only in the original "cage" and not in the surrounding solution.

If the acetoxy radical is to attack the double bond of the aromatic substituted olefin, it may do so if the olefin is adsorbed on the anode surface. In this way it could conceivably be close enough to the radical "cage" to enable the attack to occur. The adsorption of diene compounds on electrode surfaces has been reported (35).

Another mechanism proposed by Mango and Bonner (30) involves the polarization of the anodically adsorbed olefin molecules and their attack by acetate ions. The prior formation of the unstable acetoxy radicals is not required.

During the electrolysis of solutions containing 1,1-diphenylethylene and potassium hydrogen fluoride in acetic acid, the acetate ion concentration is probably sufficiently high that either of the mechanisms proposed by Mango and Bonner (30) applies.

Although no fluorine containing product was obtained during the electrolysis of KHF_2 solutions of 1,1-diphenylethylene in acetic acid, a small quantity of the butadiene $(\text{C}_6\text{H}_5)_2\text{C} = \text{CH}-\text{CH} = \text{C}(\text{C}_6\text{H}_5)_2$ which could be formed by the dehydrofluorination of $(\text{C}_6\text{H}_5)_2\text{CFCH}_2\text{CH}_2\text{CF}(\text{C}_6\text{H}_5)_2$. The latter compound was observed by Bornstein (29) as a product of the reaction of fluorinating agents with 1,1-diphenylethylene.

Apparatus

Glass apparatus was used in all of the experiments. A beaker, a U-tube and a 200-ml resin flask were used as cells.

The anode and cathode compartments were separated by glass frits, porous Teflon and alundum. The majority of the experiments were conducted in a U-tube with a medium porosity glass frit at the bottom to separate the compartments. A coarse frit allowed extensive mixing, while a fine frit provided too much resistance.

Bright platinum electrodes were used in all experiments. The source of electrical current was a series of battery eliminators.

Table 2 lists some of the runs, with the conditions prevailing during the electrolyses.

TABLE 2

<u>Run</u>	<u>KHF₂ conc.</u>	<u>DPE</u>	<u>Pot.</u>	<u>Curr.</u>	<u>Time</u>
3	13.58g/150 ml.	4.43g	8.4V	10.0-1.0 mA	79 hr.
7	2.8/100	5.3	30	50.0-15.0	18
8	2.8/100	5.12	30	80.0-10.0	24
9	Satd. (50)	5.20	30	360-90	9
13	Satd. (100)	9.0	30	650-110	49
14	Satd. (130)	7.0	30	600-100	140
16	Satd. (150)	8.0	30	230-0	23
19	Satd. (50)	1.6	20	410-200	18
22	2.8/50	5.12	30	60-15	24

The acetic acid was removed in a flask evaporator and the residue was separated by column chromatography. The products were identified by elemental analysis, infrared

spectra and melting point. Each product was compared with an authentic sample prepared by other means.

The claim by Schmidt and Schmiat* that the addition of fluorine had been achieved encourages us to continue to look at the system despite our failure to repeat their work, thus far.

The electrolyses described by Schmidt and Schmidt (2) and by Mango and Bonner (30) were not conducted under controlled potential conditions. Our work thus far has been limited to an effort to repeat the work of Schmidt. A polarographic and controlled potential investigation of the system should enable us to determine if the addition of fluorine can be accomplished in acetic acid solutions.

Preliminary coulometric investigations of the potassium hydrogen fluoride solutions in acetic acid were conducted. A rotating platinum electrode was used as an anode, with a saturated calomel electrode as reference. A Sargent model XV polarograph, without IR drop compensation, was the only instrument available.

The solutions of potassium hydrogen fluoride and potassium acetate in glacial acetic acid, which were investigated, are not highly conducting and correction for the large IR drop in the solution is desirable. The polarographic curves obtained from approximately 1M potassium

* A request to Prof. Schmidt for further information brought no reply.

acetate and 1M potassium hydrogen fluoride solutions were identical. At potentials up to +1.2 volts no current was observed. At about +1.35 volts a current was observed in both solutions. This current is most likely due to the oxidation of the solvent or of the acetate ion. When 1,1-diphenylethylene was added to the solution the polarogram showed a current which started at 0.9 v with a half-wave potential of approximately 1.2 v.

This preliminary polarographic study indicates that the 1,1-diphenylethylene is most likely the species oxidized at the lower potential. The oxidized form of the olefin may then react with acetate ions and conceivably may react with fluoride ions.

These voltammetric observations are consistent with the second mechanism proposed by Mango and Bonner (30) for the acetoxylation reaction. The attack of a polarized 1,1-diphenylethylene molecule on the surface of the anode by acetate ions or acetic acid molecules is more in keeping with the lower anodic oxidation half-wave potential. The potential necessary to form the acetoxy radicals required by first mechanism is considerably higher.

Figure 3 is a diagram of the apparatus used for the RPE voltammetry. Figures 4 and 5 indicate that the same species is being oxidized in glacial acetic acid solutions of sodium acetate and potassium hydrogen fluoride. Figure 6 shows the oxidation of the organic species at a lower

potential.

These preliminary voltammetric investigations suggest a conceivable mechanism for anodic fluorinations. The oxidized, cationic form of the diphenylethylene may react with fluoride ions. The fluorination described by Schmidt and Schmidt (1,2) could occur by this mechanism rather than the highly unlikely incipient release of fluorine.

If fluoride ions can react with oxidized species in the vicinity of the anode, a general, mild method of fluorination is possible.

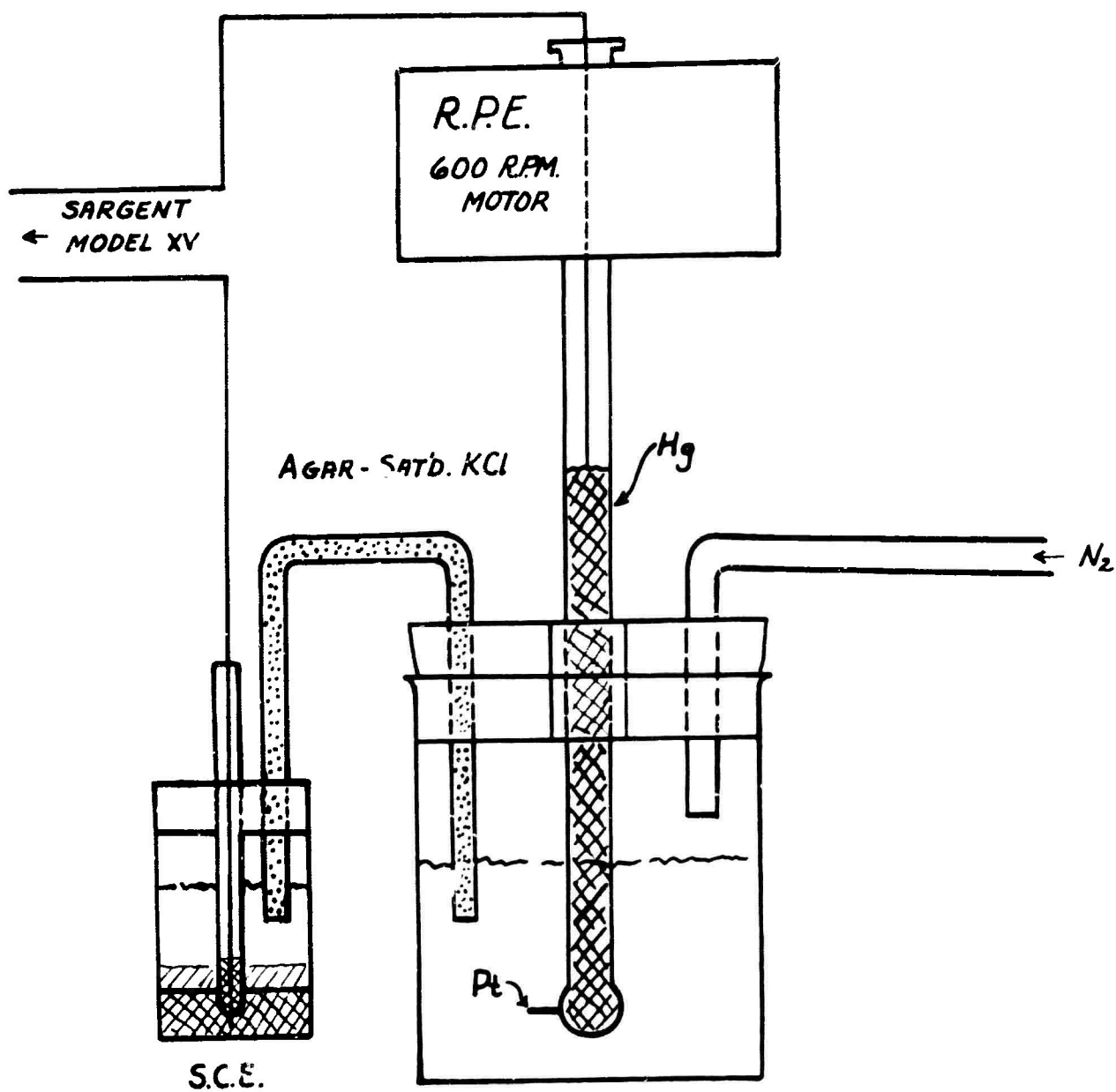


FIGURE 1

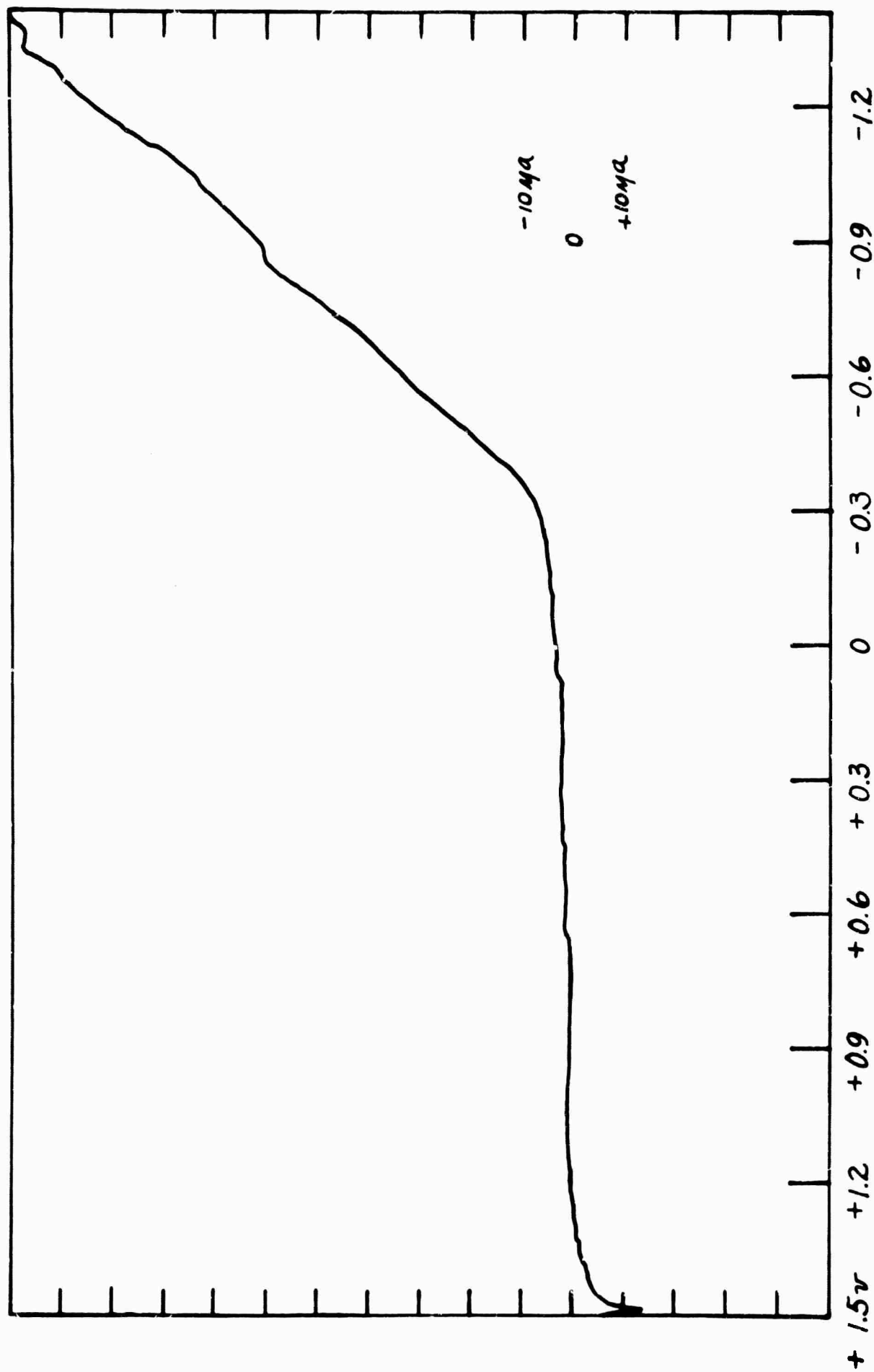


FIGURE 2

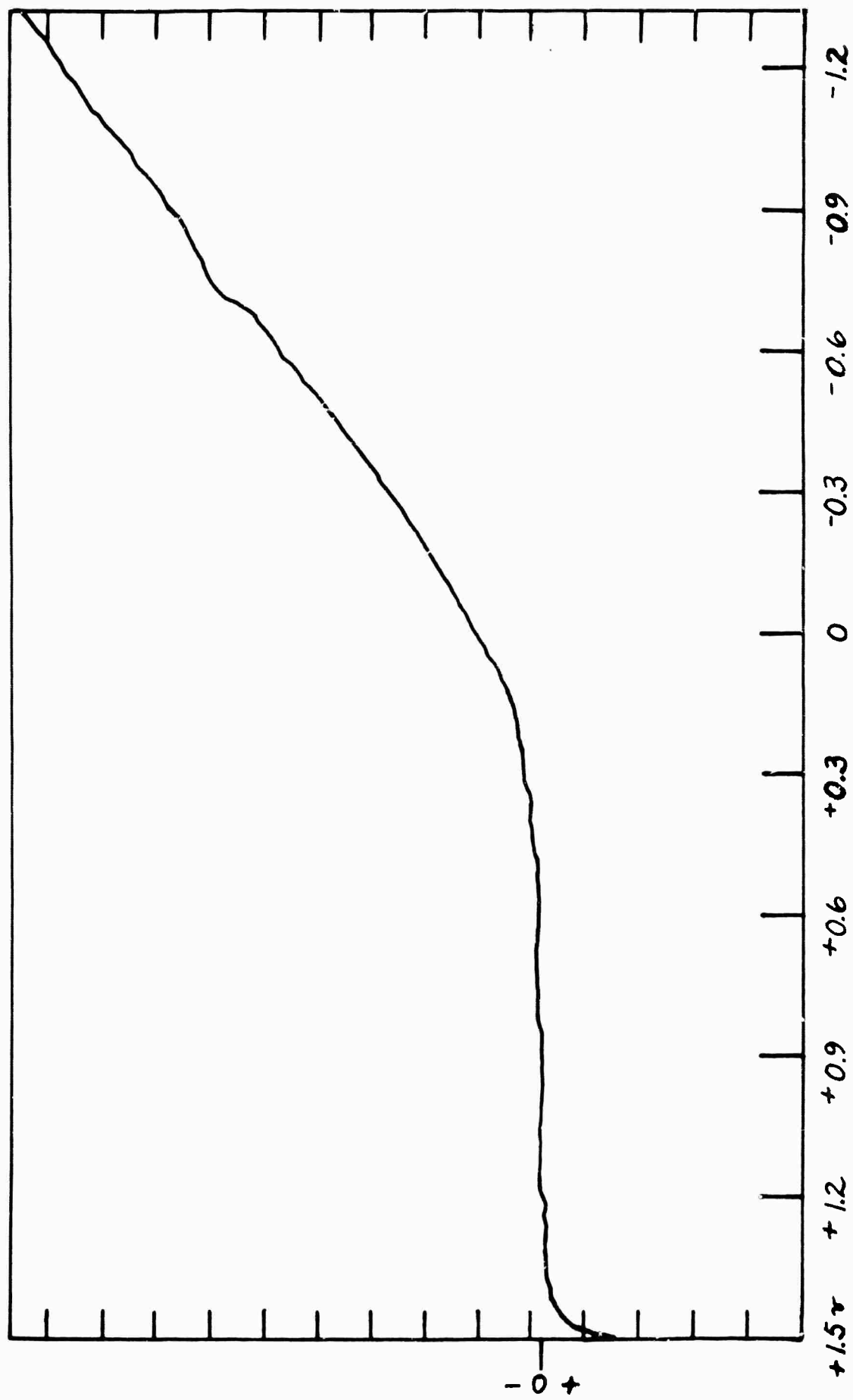


FIGURE 3

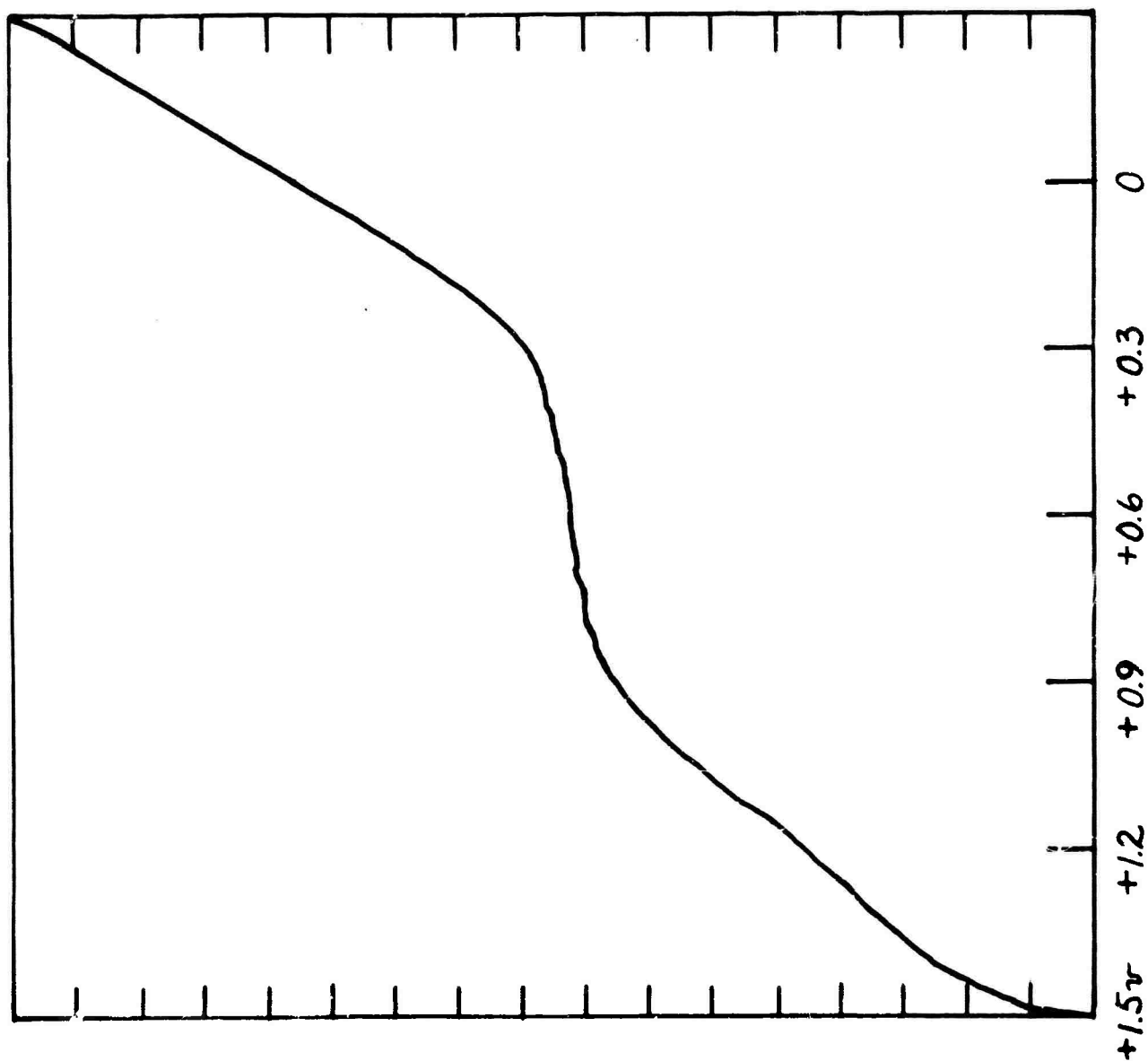


FIGURE 4

References

1. Schmidt, H. and Schmidt, H. D., Chem. Tech., 5, 454 (1953)
2. Schmidt, H. and Schmidt, H. D., J. prakt. Chem. [4], 2, 250 (1955)
3. Curtius, T. and Schulz, H., J. prakt. Chem., [2], 42, 532-3 (1890)
4. Kronberg, M. L. and Hasker, D., J. Chem. Phys., 10, 309-17 (1942)
5. Fackler, W. V., Jr., B. S. Thesis, Univ. of Illinois 1948
6. Deeley, C. M. and Richard, R. E., Trans. Faraday Soc., 50, 560-6 (1954)
7. Snyder, R. G. and Decius, J. C., J. Inorg. Nucl. Chem., 13, 280 (1959)
8. Bock, H. Z., Naturforsch., 17B, 426 (1962)
9. Deeley, C. M. and Richards, R. E., Trans. Faraday Soc., 50, 562 (1954)
10. Peterson, S. W. and Levy, H. A., J. Chem. Phys., 20, 704 (1952)
11. Snyder, R. G. and Decius, J. C. Spectrochim. Acta, 13, 280 (1959)
12. Schumb, W. C. and O'Malley, R. F., Inorg. Chem., 3, 922 (1964)
13. Bray, W. C. and Cuy, E. J., J. Am. Chem. Soc., 46, 858-75 (1924)
14. Audrieth, L. F. and Ogg, B. A., "Chemistry of Hydrazine" John Wiley & Sons, Inc., New York, 1951, p. 159
15. Caley, E. R. and Kahle, G. R., Anal. Chem., 31, 1880 (1959)
16. Ruff, O., Fischer, J. and Luft, F., Z. anorg. allgem. Chem., 172, 417 (1923)

17. Muettert, E., Ph. D. Thesis, Harvard, 1952
18. Rogers, H. H., J. Electrochem. Soc., 111, 701 (1964)
19. Schmeisser, M. and Sartori, P., Chem. Ing. Techn., 36,
9 (1964)
20. Sharp, D. W., Adv. Fluorine Chem., 1, 121 (1961)
21. S. Karp and L. Meites, J. Am. Chem. Soc., 84, 906 (1962)
22. Bard, A. J., Anal. Chem., 35, 1602 (1963)
23. Huber, F., Dissertation, Rheinisch-Westfallischen T. H.,
Aachen (1959)
24. Dimroth, O. and Bockemuller, W., Ber., 64, 516 (1931)
25. Bornstein, J. and Borden, M. R., Chem. and Ind., 1958,
441
26. Private communication
27. Fredenhagen, K. and Cadenbach, G., Ber., 67, 928 (1934)
28. Hapfgartner, K., Monatsh., 32, 523 (1911)
29. Bornstein, J., Borden, M. R., Nunes, F. and Tarlin, H. I.,
J. Am. Chem. Soc., 85, 1609 (1963)
30. Mango, F. D. and Bonner, W. A., J. Org. Chem., 29, 1367
(1964)
31. Kolbe, H., Ann., 69, 257 (1849)
32. Goldschmidt, S., Leicher, W. and Haas, H., Ann., 577, 123
1452
33. Weedon, B. C. L., Adv. Org. Chem., 1, 1 (1960)
34. Herk, L., Feld, M. and Szwarc, M., J. Am. Chem. Soc., 83,
2998 (1961)
35. Smith, W. B. and Gilde, H. G., J. Am. Chem. Soc., 81,
5325 (1959)

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Boston College Department of Chemistry Chestnut Hill, Massachusetts 02167		20. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
		20. GROUP	
3. REPORT TITLE THE MILD FLUORINATION OF NITROGEN COMPOUNDS			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Scientific Final			
5. AUTHOR(S) (First name, middle initial, last name) Robert F O'Malley Edward M McCarron Alan M Phipps Bernard M Halpin			
6. REPORT DATE 31 August 1965	7a. TOTAL NO. OF PAGES 29	7b. NO. OF REFS 35	
8a. CONTRACT OR GRANT NO. AF-AFOSR-62-464 (ARPA)		9a. ORIGINATOR'S REPORT NUMBER(S)	
b. PROJECT NO 3818-50			
c. 6251201R		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d. 681308		AFOSR 68-1244	
10. DISTRIBUTION STATEMENT 1. This document has been approved for public release and sale; its distribution is unlimited.			
11. SUPPLEMENTARY NOTES TECH, OTHER		12. SPONSORING MILITARY ACTIVITY AF Office of Scientific Research (SREP) 1400 Wilson Boulevard Arlington, Virginia 22209	

13. ABSTRACT

In an attempt to prepare tetrafluoro hydrazine, or other nitrogen fluorides, the electrolysis of molten hydrazinium difluoride led to the formation of nitrogen gas as the principal anodic product. A trace of nitrogen trifluoride was the sole nitrogen fluoride observed. In a search for a non-aqueous solvent (other than hydrogen fluoride) in which electrolytic fluorination may be conducted, it was found that the electrolysis of glacial acetic acid solutions of potassium hydrogen fluoride did not lead to fluorination, as had been previously claimed, but to acetoxylation. Thus, 1, 1-diphenylethylene gave the corresponding diacetate, not the difluoride.

The possible mechanisms for the acetoxylation involve either the attack of the unsaturated hydrocarbon by acetoxyl radicals, produced at the anode, or nucleophilic attack of cationic species, formed by anodic oxidation of the hydrocarbon. Preliminary evidence that the latter mechanism is operative supports the view that anodic fluorination in a non-aqueous solvent is feasible.

The study of the use of acetonitrile as a solvent was also begun. The absence of a suitable soluble fluoride containing electrolyte severely limited its use.

Security Classification

14

KEY WORDS

LINK A

LINK B

LINK C

NAME	ROLE
Mr. J. Edgar Hoover	Director
Mr. Clegg	Chief of Bureau
Mr. Glavin	Chief of Bureau
Mr. Ladd	Chief of Bureau
Mr. Nichols	Chief of Bureau
Mr. Rosen	Chief of Bureau
Mr. Tracy	Chief of Bureau
Mr. Carson	Chief of Bureau
Mr. Egan	Chief of Bureau
Mr. Gurnea	Chief of Bureau
Mr. Hendon	Chief of Bureau
Mr. Pennington	Chief of Bureau
Mr. Quinn	Chief of Bureau
Mr. Nease	Chief of Bureau
Mr. Gandy	Chief of Bureau

W T

[illegible]

WT

[illegible]

W T

1,1-Diphenylethylene

Security Classification